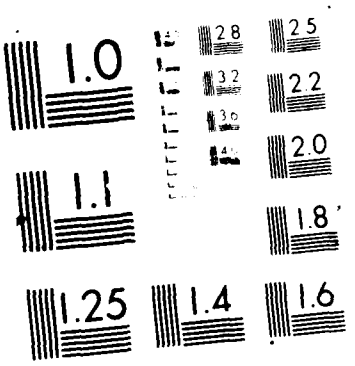
AD-A185 917 SURFACE CHEMISTRY OF CHEMICALLY SENSITIVE FIELD EFFECT TRANSISTORS(U) MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF CHEMISTRY M S WRIGHTON 22 SEP 87 1/1

UNCLASSIFIED N00014-84-K-0291 F/G 9/1 NL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## REPORT DOCUMENTATION PAGE

AD-A185 917

1b. RESTRICTIVE MARKINGS: none

3. DISTRIBUTION/AVAILABILITY OF REPORT: unlimited



2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

4. PERFORMING ORGANIZATION REPORT NUMBER(S): End of Contract Report

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION: Department of Chemistry

6b. OFFICE SYMBOL (If applicable):

7a. NAME OF MONITORING ORGANIZATION: Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code): Massachusetts Institute of Technology, 77 Mass. Avenue, Bldg. 6-335, Cambridge, MA 02139

7b. ADDRESS (City, State, and ZIP Code): Chemistry Division, 800 Quincy Street, Arlington, VA 22217

8a. NAME OF FUNDING/SPONSORING ORGANIZATION: Office of Naval Research

8b. OFFICE SYMBOL (If applicable):

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: N00014-84-K-0291

8c. ADDRESS (City, State, and ZIP Code): Chemistry Division, 800 Quincy Street, Arlington, VA 22217

10. SOURCE OF FUNDING NUMBERS

| PROGRAM ELEMENT NO. | PROJECT NO. | TASK NO. | WORK UNIT ACCESSION NO. |
|---|---|---|---|
| | | | 202-261 |

11. TITLE (Include Security Classification): Surface Chemistry of Chemically Sensitive Field Effect Transistors

12. PERSONAL AUTHOR(S): Mark S. Wrighton

| 13a. TYPE OF REPORT | 13b. TIME COVERED | 14. DATE OF REPORT (Year, Month, Day) | 15. PAGE COUNT |
|---|---|---|---|
| Final | FROM 4/17/84 TO 11/30/86 | 9/22/87 | 9 |

16. SUPPLEMENTARY NOTATION

| 17 COSATI CODES | | | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) |
|---|---|---|---|
| FIELD | GROUP | SUB-GROUP | microelectrochemistry, microelectronics, chemically sensitive surfaces |
| | | | |
| | | | |

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This report hightlights the research accomplishments in connection with studies of microelectrochemical devices including transistors and diodes. A bibiliography of published work in connection with the contract is included.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT: ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION: unclassified

| 22a. NAME OF RESPONSIBLE INDIVIDUAL | 22b. TELEPHONE (Include Area Code) | 22c. OFFICE SYMBOL |
|---|---|---|
| Mark S. Wrighton | 617-253-1597 | |

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

FINAL TECHNICAL REPORT - SEPTEMBER 10, 1987

TITLE: "SURFACE CHEMISTRY OF CHEMICALLY SENSITIVE FIELD EFFECT TRANSISTORS"

CONTRACT NO. N00014-84-K-0291

WORK UNIT NO. 202-261

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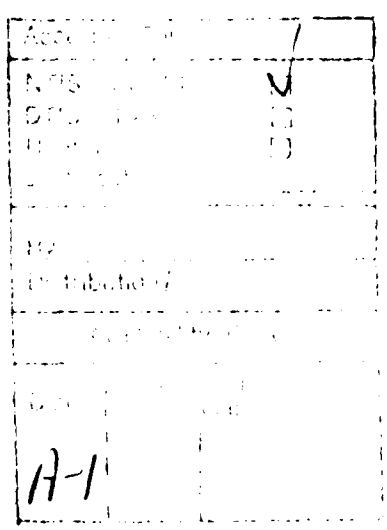
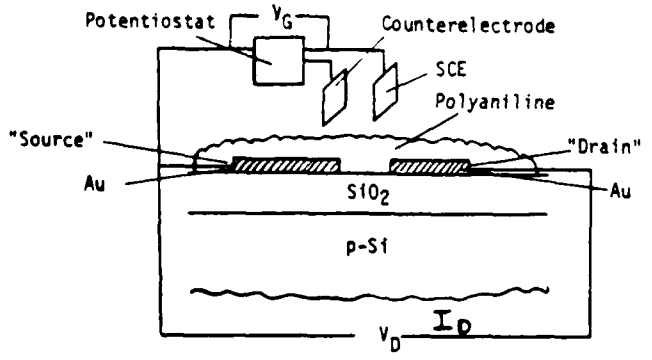


Summary of Research Accomplishments

Research conducted with support in connection with the contract led to the development of microfabrication capability in the Wrighton group at M.I.T. The microfabricated structures designed and prepared by the Wrighton group led to the demonstration of the first molecule-based transistors and diodes. The publications resulting from the research are listed below, and the following paragraphs summarize the highlights of the accomplishments.

Conducting Polymer-Based Transistors. Scheme I illustrates the kind of transistor device pioneered by the Wrighton group where the crucial feature stems from variation in the state of charge of the polymer contacting the two microstructures (Au or Pt) labelled "Source" and "Drain". Variation in the state of charge of the polymer is effected by changing the electrochemical potential, $V_G$. The overall function is that change in $V_G$ results in change in the drain current, $I_D$, between source and drain at fixed drain potential, $V_D$. Conducting polymers such as polypyrrole, poly(N-methylpyrrole), poly(3-methylthiophene), and polyaniline show dramatic changes in conductivity upon changes in their state of charge from $V_G$ variations of ~0.5 V. Research has shown that these polymers can be electrochemically grown onto two microelectrodes as illustrated in Scheme I.

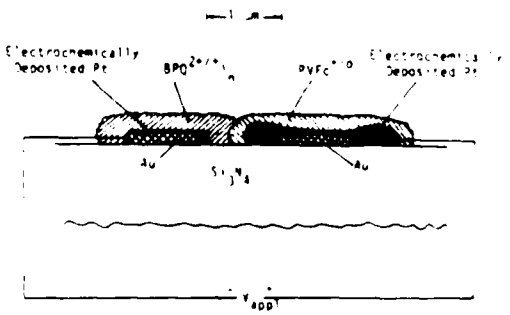



Scheme I. Molecule-based transistor where $I_D$ can be turned on and off by electrically driven changes in the state of charge of the redox polymer connecting source and drain.

The conducting polymer-based transistors function in a manner analogous to solid state devices: variation in $V_G$ results in modulation of $I_D$. However, the polymer-based devices require oxidation/reduction chemistry, meaning that the movement of ions into or out of the polymer must occur upon current flow in the gate circuit, $I_G$, from variation in $V_G$. In solid state devices $I_G$ is only capacitive current, whereas in the polymer-based device most of the $I_G$ is faradaic current. The conclusion is that the polymer-based device will be slower thant the solid state device, because ion mobility is much lower than electron mobility. Nonetheless, the conducting polymer-based devices show power gain at frequencies below $10^3$ Hz for a source-drain separation of ~1.5 μm.

Conventional Redox Polymer-Based Devices. The molecule-based transistors are three terminal devices and involve the use of a single redox polymer. In principle, any redox material could be used, but so-called conducting polymers give large $I_D$'s and relatively fast switching compared to conventional redox polymers. However, conventional redox polymers--- materials based on discrete redox active molecular centers--- do have sufficient "conductivity" changes to be interesting in connection with microelectrochemistry.

One interesting microelectrochemical device that has been demonstrated using two conventional redox polymers is a two-terminal device, a diode, illustrated in Scheme II. The two different polymers empolyed




Scheme II. A two-terminal diode based on the modification of two adjacent microelectrodes with two different redox polymers having a different formal potential.

are polyvinylferrocene and a polyviologen having $E^{\circ\prime}$'s at +0.45 and -0.55 V vs. SCE, respectively. The ~1.0 V difference in $E^{\circ\prime}$'s for these redox polymers means that the cross redox reaction occuring at the polyvinylferrocene/-polyviologen interface is, in effect, unidirectional. Thus, when the negative lead is applied to the polyviologen-coated microelectrode and the positive lead is attached to the polyvinylferrocene contact current will flow when the applied potential exceeds ~1.0 V. The microelectro-chemical diode does rectify current, but the low "conductivity" of the polymers connecting the two microelectrodes limits the magnitude of the maximum current. Moreover, the switching time is of the order of seconds for a 1.5 μm spacing between contacts.

Microelectrochemical Sensors. The switching time of microelectrochemical transistors and diodes demonstrated so far rules out many applications traditionally associated with such devices. However, the electrical characteristics of the microelectrochemical devices are intrinsically chemically sensitive. This leads to the possibility of developing new kinds of sensors for chemical and biological substances. Demonstrations of proof-of-concept for microelectrochemical devices for monitoring $H_2$, $O_2$, and pH in aqueous solution have been discussed in publications listed below.

Technical Reports.

"Chemical Derivatization of an Array of Three Gold Microelectrodes with Polypyrrole: Fabrication of a Molecule-based Transistor", H.S. White, G.P. Kittlesen, M.S. Wrighton J. Am. Chem. Soc., 1984, 196, 5375.

"Chemical Derivatization of Microelectrode Arrays by Oxidation of Pyrrole and N-Methylpyrrole: Fabrication of Molecule Based Electrode Devices", G.P. Kittlesen, H.S. White, M.S. Wrighton J. Am. Chem. Soc., 1984, 106, 7389.

"Prospects for a New Kind of Synthesis: Assembly of Molecular Components to Achieve Functions" M.S. Wrighton Comments Inorg. Chem., 1985, 4, 269.

"Resistance of Polyaniline Films as a Function of Electrochemical Potential and the Fabrication of Polyaniline-based Microelectronic Devices", E.W. Paul, A.J. Ricco, M.S. Wrighton J. Phys. Chem., 1985, 89, 1441.

"A Two-Terminal Microelectrochemical Diode with Contact Spacing of About One Micron: A Device Based on One Solution Redox Couple and One Electrode-Confined Redox Couple", G.P. Kittlesen, M.S. Wrighton J. Molec. Electronics, 1986, 2, 23.

"Poly-3-Methylthiophene Coated Electrodes: Optical and Electrical Properties as a Function of Redox Potential and Amplification of Electrical and Chemical Signals using Poly-3-Methylthiophene-based Microelectrochemical Transistors", J.W. Thackeray, H.S. White, M.S. Wrighton J. Phys. Chem., 1985, 89, 5133.

"A Microelectrochemical Diode Based on the Connection of Two Microelectrodes Using Dissimilar Redox Polymers: A Two Terminal Electrochemical Device with Submicron Contact Spacing", G.P. Kittlesen, H.S. White, M.S. Wrighton J. Am. Chem. Soc., 1985, 107, 7373.

"Digital Simulation of the Measured Electrochemical Response of Reversible Redox Couples at Microelectrode Arrays: Consequences Arising from Closely Spaced Microelectrodes", A.J. Bard, J.A. Crayston, G.P. Kittlesen, T.V. Shea, M.S. Wrighton Anal. Chem., 1986, 58, 2131.

"Chemically Responsive Microelectrochemical Devices Based on Platinized Poly(3-Methylthiophene): Variation in Conductivity with Variation in Hydrogen, Oxygen or pH in Aqueous Solution", J.W. thackeray, M.S. Wrighton J. Phys. Chem., 1986, 90, 6674.

"Modification of Microelectrode Arrays: New Microelectrochemical Devices for Sensor Applications" M.S. Wrighton, J.W. Thackeray, M.J. Natan, D.K. Smith, G.A. Lane, D. Belanger [Prepared for publication in Philosphical Transactions of the Royal Society, Series B, in connection with the Royal Society Discussion Meeting on "Biosensors", May 28-29, 1986]

"pH-Sensitive $WO_3$-Based Microelectrochemical Transistors" M.J. Natan, T.E. Mallouk, M.S. Wrighton J. Phys. Chem., 1987, 91, 648.

"Amplification of Electrical Signals with Molecule-based Transistors: Power Amplification up to a Kilohertz Frequency and Factors Limiting Higher Frequency Operation", E.P. Lofton, J. W. Thackeray, M.S. Wrighton J. Phys. Chem., 1986, 90, 6080.

"Microelectrochemical Transistors Based on Electrostatic Binding of Electroactive Metal Complexes in Protonated Poly(4-Vinylpyridine): Devices that Respond to Two Chemical Stimuli", D. Belanger, M.S. Wrighton Anal. Chem., 1987, 59, 1426.

"pH-Sensitive $Ni(OH)_2$-based Microelectrochemical Transistors" M.J. Natan, D. Belanger, M.K. Carpenter, M.S. Wrighton J. Phys. Chem., 1987, 91, 1834.

Salient Unanswered Questions.

The research program has provided proof-of-concept results relating to the rational design, fabrication, and characterization of microelectrochemical transistors and diodes. There remains many significant issues that require additional basic research effort. Such questions include the following. What fabrication and characterization methods are applicable to substantially sub-micronmicroelectrodes? Which molecular materials will give the fastest switching? Can chemically specific devices be rationally designed? What circumstances will promote rapid charge transport across metal/polymer and polymer/polymer interfaces? Answering these and other questions relating to the surface chemistry of microfabricated structures will be among the objectives of chemistry research to be pursued by the Wrighton Research Group.

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